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PROGRESS REPORT  
for the period  
January 15, 1965 - September 15, 1965

Grant NsG-117-61

FACILITY FORM 602	<u>N 66-80074</u>	<u>(THRU)</u>
	<u>(PAGES)</u>	<u>(CODE)</u>
	<u>(NASA CR OR TMX OR AD NUMBER)</u>	<u>(CATEGORY)</u>

To  
National Aeronautics and Space Administration  
Washington, D. C.

## DISPERSION STRENGTHENED SYSTEMS

This report, due to delays, covers the eight month period to September 15, 1965.

Research and development programs may be summarized under the following titles:

1. Improved Structural Stability of Ni-ThO<sub>2</sub> and Ni-Mo-ThO<sub>2</sub> Alloys Produced by Selective Oxide Reduction
2. The Role of Stored Energy and Recovery on the Properties of Oxide Dispersion Strengthened Iron
3. Structure Control on the Strength and Ductility of Fe-BeO Alloys
4. Oxide Dispersion Strengthened Niobium Alloys
5. High Volume Intermetallic Compound-Ductile Binder Composite Alloys
6. Mechanism of Deformation and Fracture in Oxide Dispersion Strengthened Alloys
7. Oxide Dispersion Strengthened Alloys by Surface and Internal Oxidation Processes
8. Regarding Internal Oxidation Processes

During this period the following publications were processed:

1. "ThO<sub>2</sub> Dispersion-Strengthened Ni and Ni-Mo Alloys Produced by Selective Reduction" by J. G. Rasmussen and N. J. Grant: Powder Metallurgy, Vol. 8, No. 15, 1965, p. 92.
2. "Alumina Dispersion-Strengthened Copper-Nickel Alloys" by Michio Yamazaki and N. J. Grant: Trans. AIME Met. Soc., 233, No. 8, 1965, p. 1573.
3. "Dispersion Strengthening" (Chapter) by N. J. Grant: to be included in publication of Proceedings of the Eleventh Sagamore Army Materials Research Conference on Strengthening Mechanisms in Metals, by Syracuse University Press, 1965.
4. "Aluminide-Ductile Binder Composite Alloys: by J. S. Benjamin and N. J. Grant: Submitted for publication to AIME Met. Soc.
5. "Oxide Dispersion Strengthened Niobium" by Diane Margel and N. J. Grant: (to be published).
6. "The Role of Cold Work and Recovery in Oxide Dispersion Strengthened Iron" by A. S. Bufferd and N. J. Grant: (to be published).

7. "Titanium Carbide Dispersion Strengthened Nickel" by R. J. Murphy and N. J. Grant: to be published.

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## RESULTS

### 1. Improved Structural Stability of Ni-ThO<sub>2</sub> and Ni-Mo-ThO<sub>2</sub> Alloys Produced by Selective Oxide Reduction

The previous progress report carried a detailed description of the processing of the alloys and will not be repeated.

These alloys were prepared from approximately 0.2 micron NiO and MoO<sub>3</sub> on to which ThO<sub>2</sub> was deposited via thermal decomposition of thorium nitrate. Extra precautions were taken to avoid reoxidation of the ultra-fine Ni and Mo reduced powders during cold compaction, and in the canning operation.

The resultant extrusions, performed at a low extrusion ratio, appeared to have a suitable fine ThO<sub>2</sub> dispersion. These alloys were given a series of cold working operations, with and without intermediate annealing treatments, to increase the level of stored energy. Evaluation of the structural stability was by means of annealing treatments at increasing temperatures, for 1 and 5 hours, by means of room temperature tension tests, and by creep rupture tests at 982°C.

In spite of improved hardness maintenance by the Ni-ThO<sub>2</sub> alloy with increasing temperature (to 1200°C), in the as-extruded condition, subsequent cold working treatments did not increase the high temperature strength to expected values. Softening occurred near 982°C.

The Ni-Mo-ThO<sub>2</sub> alloy showed low potential for cold work and failed after about 30% cold work regardless of processing treatments.

Thus, in spite of apparent satisfactory oxide dispersions, and attempted improvements in processing, these two new alloys did not yield 982°C creep rupture properties as good as those reported by Rasmussen and Grant (see above). Further checks of the system indicated that reoxidation of the ultra-fine metal powders did occur, probably due to faulty welding of the can prior to extrusion. The approximately 0.2 micron powders are extremely reactive and must be protected completely at all stages of the processing.

Fortunately, adequate quantities of the 0.2 micron NiO and MoO<sub>3</sub> remain and these will be processed once more in an effort to avoid all sources of contamination. These alloys are now in process and should be tested by the end of 1965.

### 2. Oxide Dispersion Strengthened Niobium Alloys

At the end of the previous period, it had been observed that the Nb-Al<sub>2</sub>O<sub>3</sub> alloys had extruded readily whereas the Nb-ThO<sub>2</sub> alloys were brittle and rattle-snaked during extrusion. Subsequent examination of the structures showed that there had been agglomeration of the Al<sub>2</sub>O<sub>3</sub>, leading to a coarse interparticle spacing and easy working. The more refractory ThO<sub>2</sub> remained in a finer state of distribution but was found to be located around the original surfaces of the relatively coarse niobium hydride powder particles. This led to greater difficulty in achieving hot plasticity and extensive cracking occurred during extrusion.

The conclusions reached from this study, which will appear in published form shortly, are:

- a) Dispersion strengthening could be achieved with an oxide as stable as  $\text{ThO}_2$  or  $\text{ZrO}_2$ ;  $\text{Al}_2\text{O}_3$  is not sufficiently inert to niobium and some reduction of  $\text{Al}_2\text{O}_3$  takes place.
- b) Significant further comminution of the NbH is necessary to try to achieve about 1 micron particles (as compared to 6 to 7) for significant strengthening.
- c) A stiffer canning material than steel should be used during extrusion of the Nb-Metal Oxide alloy.
- d) Because of the reactivity of one micron niobium, extreme precautions will be necessary in handling such fine powders, after decomposition of the hydride.

## 2. The Role of Stored Energy and Recovery on the Properties of Oxide Dispersion Strengthened Iron

Since the early work of Cremens and Grant, which indicated a potential for improvements in strength due to cold work of oxide dispersion strengthened alloys, extensive work in the USSR has expanded on the potential for additional cold work after hot extrusion or hot forging. Tracey and Worn, in Great Britain, then demonstrated the large potential for cold work low oxide alloys of lightly hot worked structures; their work in particular placed emphasis on the important role of intermediate annealing treatments after 5 to 15 percent reduction by cold deformation. Such processing has since been adapted to the strengthening of TD-Ni and other alloys.

Nevertheless all the factors involved in these processing steps were not well understood. The variables of interest include volume content of oxide (or interparticle spacing), extrusion ratio, extrusion temperature, amount of cold work per step, time and temperature of the intermediate anneal.

In this research program, iron was selected as the base because one could extrude at any desired ratio above or below the alpha to gamma transformation and thereby retain or completely eliminate cold work of extrusion. The oxides were alpha and gamma  $\text{Al}_2\text{O}_3$  and  $\text{ThO}_2$ .

The results indicated that:

- a) Use of low extrusion ratios is important primarily in low oxide volume alloys. If, for a given fine oxide particle size, the oxide content is high (7 to 15 percent) the interparticle spacing will be small and the alloy will have low capacity for subsequent cold work. Cracking will occur prematurely because of innate low ductility characteristics.
- b) At low oxide content (1 to 4 volume percent), low extrusion ratios can be utilized because subsequent cold work can be applied to the ductile structure. In such cases not only do low and high temperature strength values increase, but ductility also increases.

c) For a 2 to 3 volume percent oxide alloy as many as 10 steps (or more) of 10 percent reduction of area can be utilized without cracking, but intermediate annealing treatments are necessary.

d) The annealing treatments can be carried out over a rather wide temperature range, provided that one is well above the minimum recrystallization temperature of the metal or alloy. For iron this would be 700 to about 1000°C. If recrystallization occurs, the structure can be damaged. Time is of lesser importance.

e) Of great importance, but as yet poorly understood, is the distribution of strain energy in the alloy. Apparently the intermediate annealing treatments are capable of polygonizing the structure between oxide particles without removing the dislocation tangles around the particles.

This work is now being prepared for publication and preprints should be available within about six weeks.

#### 4. Structure Control on the Strength and Ductility of Fe-BeO Alloys

It had been indicated both from previous work and recent preliminary experiments that while iron could be beneficially oxide dispersion strengthened using  $Al_2O_3$ , MgO and  $ThO_2$ , none of the alloy systems was fully optimized.

It is a fact, however, that the maximum number of applications will always be in iron and iron base alloys, making it desirable to do further work in iron alloys to optimize structure and properties.

It had been shown that Fe- $Al_2O_3$  (gamma) alloys at 650°C were 2 to 3 times stronger for a 100-hour rupture life than any of the 400 series stainless steels or 304 stainless steel; however, exposure to higher temperatures resulted in conversion to alpha  $Al_2O_3$  with partial loss of properties. Further, it was observed that there was frequent contamination of the  $Al_2O_3$  by unreduced iron oxides, leading to spinel ( $FeO.Al_2O_3$ ) structures and poorer properties.

Similarly MgO was a good dispersoid but reacted too readily with moisture to give high strength values at 650°C.

$ThO_2$  is quite stable normally, but also absorbs water from the atmosphere. This increases the iron oxide content and often leads to low properties. Further  $ThO_2$  is both heavy and expensive. Thus BeO appeared to be an attractive choice, especially in view of its extreme stability. The problem was how best to achieve the finest possible dispersion in a reproducible manner.

For this program several processes have been investigated. As of now the approaches which appear most attractive are:

a) internal oxidation: a large series of trials have been run in an effort to establish the  $H_2O:H_2$  ratio which will give the best oxygen pressure for oxidation of the Be to BeO. These tests are continuing. Previously one utilized the oxygen pressure derived from decomposition of oxides such as  $Cu_2O$ , FeO, NiO, etc.

b) Selective reduction in a mixture of  $\text{Fe}_3\text{O}_4$  and  $\text{BeO}$ : the relative softness of iron oxide permits easy comminution to 0.2 to 0.5 micron. Reduction of iron oxide is readily accomplished at relatively low temperatures, without danger of spinel formation with the  $\text{BeO}$ , as was the problem with  $\text{Al}_2\text{O}_3$  dispersions.

b) Beryllium salt decomposition onto iron oxide: this process permits production of 0.01 to 0.05 micron  $\text{BeO}$  from available salts, onto 0.2 to 0.5 micron iron oxides. The process is attractive because of similar prior experience with  $\text{NiO} - \text{ThO}_2$  and  $\text{NiO} - \text{MoO}_2 - \text{ThO}_2$  systems.

Tests have been under way on these and other systems; two will be selected within the next month or two for alloy production and testing.

#### High Volume Intermetallic Compound - Ductile Binder Composite Alloys

Details of this work were extensively reported in the previous progress report and will not be repeated.

Also a technical report has been submitted to the AIME for publication and preprints have been submitted to NASA. Only the conclusions will be repeated below.

a) A reasonable approximation of the optimum cermet structure can be achieved by powder metallurgy techniques plus hot extrusion provided that the hard refractory phase is coated with the ductile binder phase prior to extrusion.

b) The high temperature strength values of the  $\text{CoAl}$  and  $\text{Ni}_3\text{Al}$  based composites are greater than those of the pure refractory hard phases due, in part, to added benefits of oxide dispersion strengthening and retained cold work of extrusion.

c) Stress rupture strength values at  $982^\circ\text{C}$  are good. Alloys with about 50 percent binder are in all cases stronger than the pure hard phase. Binder materials should be either alloyed to near equilibrium saturation values or based on higher melting temperature materials to slow down diffusion rates and thereby decrease phase interactions and structure instability.

d) The oxidation resistance of the alloys produced in this study was outstanding, and at  $982$  and  $1094^\circ\text{C}$  was 5 to 10 times better than was measured for 80 Ni - 20 Cr alloys.

e) The room temperature stress - strain characteristics of  $\text{CoAl}$  and  $\text{Ni}_3\text{Al}$ -based composites were similar to those of conventional  $\text{TiC}$  and  $\text{WC}$  based cermets.

f) Single phase alloys of both  $\text{NiAl}$  and  $\text{Ni}_3\text{Al}$  exhibit up to 1.5 percent plastic elongation at fracture in room temperature tests.

g) The results of room temperature bend tests suggest that microstructure and the presence of phase boundaries are more important than the bulk properties of the phases themselves.

## 6) Mechanisms of Deformation and Fracture of Oxide Dispersion Strengthened Alloys

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In spite of considerable work on oxide dispersion strengthened alloys over a period of 15 years, we are not today able to classify the deformation mechanisms or fracture modes. The roles of slip and grain and subgrain boundary shear have not been studied; migration of boundaries has not been observed.

It is the purpose of this phase of the program to seek answers and to classify deformation and fracture behavior.

Internal oxidation of Cu-Al alloys is planned to yield various amounts of oxide content, interparticle spacing, etc. Alloys for the study, vacuum melted, have been received and converted into fine machine milled chips. In turn these chips are being converted into near micron powders (flake shape) for subsequent internal oxidation. Volume content of oxide, particle size and interparticle spacing will be established in each case. Particle spacings up to 2 microns are planned to simplify metallographic and X-ray studies.

Alloys with and without subsequent cold work will be compared for mechanical behavior. The internal oxidation steps are now in process.

In addition an effort will be made to produce very coarse grained foil or sheet of similar composites (these alloys are on hand) to endeavor to selectively internally oxidize grains and grain boundaries. Behavior with and without cold work will be studied. In this way the contributions of oxides to grain versus grain boundary stability will be determined for optimization of structure.

## 7) Oxide Dispersion Strengthened Alloys by Surface and Internal Oxidation Techniques

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It has been thought for too long that the Al-Al<sub>2</sub>O<sub>3</sub> SAP structure is unique in this family of alloys. Actually proper concentrations of a readily oxidizable element in relatively dilute solution should permit surface oxidation of fine powders. With flake powders, or with SAP, the surface area is extremely large and significant contributions to oxide content may be expected.

This project, just now underway, will examine the systems Cu-Al<sub>2</sub>O<sub>3</sub> and Cu-Ni-Al<sub>2</sub>O<sub>3</sub>. By producing submicron powders, oxide content of practical significance may be achieved (1 - 2 percent). By combination of surface oxidation plus internal oxidation further improvements are expected.

The alloy powders are on order. They will be comminuted by attrition techniques to produce the submicron size powders.

## 8) Regarding Internal Oxidation

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Internal oxidation of copper alloys (by Preston and Grant) has been the strongest and most stable copper alloys to date. Superalloys and nickel have been relatively poorer in performance. Studies of a series of dilute solutions of Cr, Ti, Al, and Be in nickel gave about 10% internal



depth of oxide penetration with time, temperature and composition; change in oxide particle size with depth of penetration; differences in average oxide particle size for the different solute elements; and differences in oxide size variation with composition.

These studies were not completed about two years ago due to the departure of the principle investigator. That gentleman is now with us again, and will complete this fascinating and important study so that major improvements in oxide dispersion strengthened nickel alloys can be pursued. The program is just now being reactivated.